

Correlation between early-stage expansion and spectral emission of a nanosecond laser-induced plasma from organic material

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ABSTRACT

Laser-Induced Breakdown Spectroscopy (LIBS) has been used since 40 years on typical samples such as metals, alloys, rocks. Detection of organic hazards or analysis of biological compounds under atmospheric pressure with LIBS represents a new challenge. For this purpose, we need better understandings of the physico-chemical properties of the plasma in atmosphere and their influences on the LIBS signal.

As a model sample of organic materials, Nylon 6-6 has been studied under nanosecond ablation at different wavelengths (1064 nm and 266 nm) and energies (from 1 to 5 mJ) in order to observe the influence of these parameters. Shadowgraph technique is used to image the plasma at its early stage of expansion (0 to 40 ns). Time-resolved LIBS signal is recorded for longer times (50 ns to 5 μ s).

In the infrared regime, the expansion of the plume is faster along the laser axis, perpendicular to the sample surface. On the contrary, for UV ablation, the expansion of the plume is quite isotropic. We can also observe different regimes of expansion due to Laser-Supported Detonation Waves (LSDW) above 3 mJ in the UV regime.

In particular, these observations provide us ideas to understand the kinetics of the CN emission in the LIBS signal. In the IR regime, a formation of CN due to carbon present in the sample and nitrogen in the air via the reaction $2C + N_2 \rightarrow 2CN$ can be observed. In the UV regime, the direct ablation of CN bonds is clearly seen but other effects like screening and recombination due to LSDW have also been observed.

KEYWORDS

Polymer ablation, Shadowgraphy, Time-resolved laser induced breakdown spectroscopy, Plasma chemistry, Organic materials analysis, Expansion of laser-induced plasma

1 INTRODUCTION

Laser-Induced Breakdown Spectroscopy (LIBS) traditionally deals with solid materials since its initial demonstration in 1963¹. As an analytical technique, it's crucial to have a good performance in quantitative or semi-quantitative analysis. So, the search of the stoichiometric ablation² is an important issue because it makes the plasma fully representative of the composition of the sample. Furthermore, models and numerical codes have been developed to extract quantitative information from the plasma emission³. For simple materials, as metals, alloys and semi-conductors, LIBS is efficient enough to give the correct concentrations of the major and minor elements. Recently, the extension of the LIBS technique to organic and biological samples is needed because application such as analysis of trace elements in vegetables or detection of bio-threats, ...⁴. However the extension of the LIBS technique to organic samples under reactive atmosphere like ours (mix of nitrogen and oxygen) implies a more complex plasma chemistry. For example, one of these difficulties is the interpretation of the emission from CN radicals in the plasma since such emissions can be due to native CN bonds as well as the recombination of atomic carbon (C) or diatomic carbon (C₂) with molecular nitrogen (N₂) in the air⁵.

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In this paper, we present the results of an experimental study dedicated to the understanding of the processes leading to the ablation and the plasma emission from an organic sample. In this study, the early stage of expansion of the plasma (0 to 40 ns) was investigated by the shadowgraph technique⁶, in order to analyze the plasma hydrodynamics before and at the beginning of the spectroscopic emission that we consequently measure by time-resolved LIBS. The sample is Nylon 6,6, used as a model sample because it contains a carbon chain and CN bonds. This study is made in nanosecond regime of ablation, and by varying the pulse wavelength and its energy. The different ablation regimes between UV and IR pulses are studied with different laser pulse energy. The correlations between ablation regimes, expansion of the plasma and its spectral emission are observed.

2 EXPERIMENTAL SETUP

2.1 Shadowgraph setup

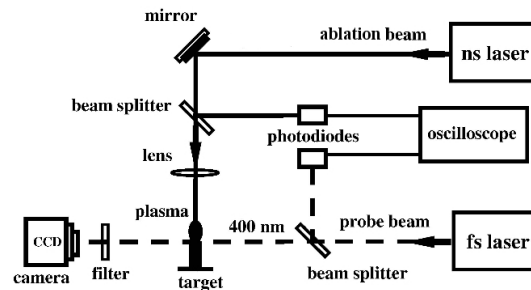


Figure 1. Shadowgraph setup

In Figure 1, we show the Shadowgraph setup that we used in Lawrence Berkeley National Laboratory for our experiments. The ablation laser is a Nd:YAG laser which delivered 1064 nm or 266 nm pulses with energy per pulse from 1 to 5 mJ and of pulse duration of 4 ns. The pulses are focused by a quartz lens to a spot with a diameter of 100 μm .

The probe laser is a Ti:Sa femtosecond laser delivering 100 fs pulses at 800 nm. The CCD camera being sensitive to visible spectrum, this beam is doubled by a KDP crystal to 400 nm. The camera is a CCD camera (Nikon D200). The target is a sample of Nylon 6,6. The ablation is made on the thinner part of it in order to have a cleaner image of the plasma. Each shot is a made on a fresh surface.

The delay between the ablation pulse and the probe pulse is precisely measured using two photodiodes.

2.2 Time-resolved LIBS setup

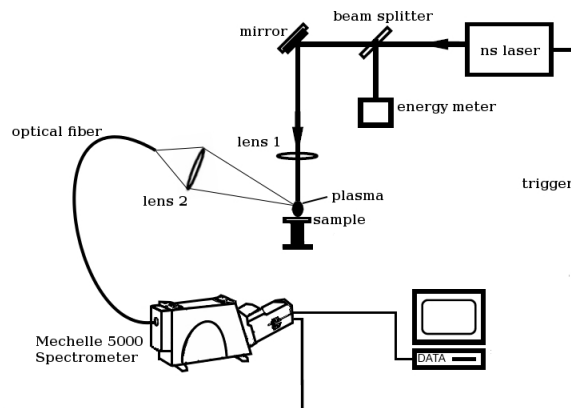


Figure 2. Time-Resolved LIBS setup

In Figure 2, we see the time-resolved LIBS setup. The ablation laser delivers 5 ns pulses at a repetition rate of 10 Hz. We vary (as for the shadowgraph experiment) the wavelength and the pulse energy. The pulse is focused with a

quartz lens to a 100 μm spot. The plasma emission is collected by a quartz lens with an angle of about 45° with respect to the laser axis. The collected light is focused on a quartz-core fiber and coupled to an Echelle spectrometer equipped with an iCCD camera. This spectrometer allows a wide range detection (200-900 nm) with a high precision (40 pm at 200 nm to 200 pm at 1000 nm).

The plasma emission is detected with a detection window of 50 ns duration and with a varying delay time with respect to the impact of the laser pulse on the sample. Thanks to this method we can follow the kinetics of the signal with a resolution of 50 ns.

3 RESULTS AND DISCUSSION

3.1 Shadowgraph

3.1.1 Infrared regime of ablation

On the figure 3, we see the evolution of the shockwave after the ablation of Nylon 6,6 by a 4 ns IR pulse at 3 mJ.

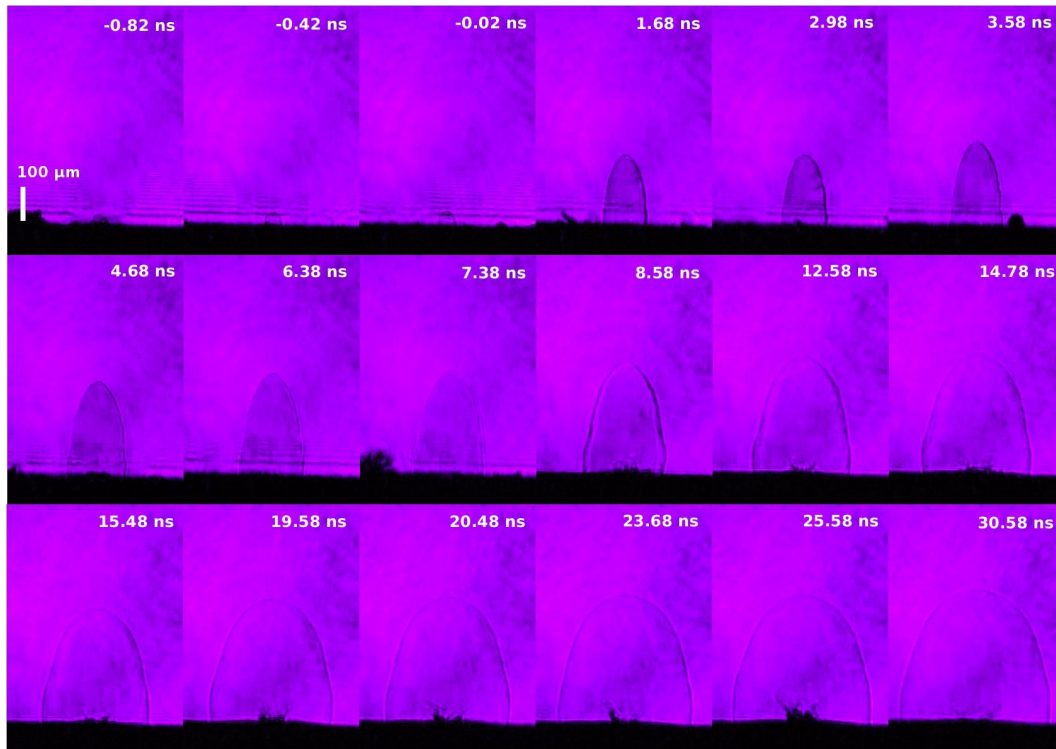


Figure 3. Time evolution of the laser induced plasma shockwave (pulse duration: 4 ns, wavelength: 1064 nm, energy: 3 mJ)

We can notice the anisotropy of the expansion of the shockwave with a faster velocity along the perpendicular axis to the sample surface. We can explain this anisotropy by the interactions between the laser pulse and the plasma. The shockwave is observed as composed by two parts. The main part expands as soon as the ablation starts consequently to the absorption of the laser pulse by the sample. The second part results from the absorption of the tailing part of the laser pulse by the main shockwave. It corresponds to the Laser-Supported Combustion Wave (LSCW). This second part of the shockwave, heated by the laser through plasma absorption, has a larger expansion velocity.

3.1.2 Ultraviolet regime of ablation

We can see with the figure 4 the time evolution of the shockwave due to the ablation of Nylon 6,6 by a UV nanosecond pulse (266 nm, 4 ns, 3 mJ). Contrary to the IR regime, the expansion of the shockwave is spherical. This phenomenon is easy to understand as the consequence of a symmetric expansion of the plasma into an homogeneous

atmosphere. However, above 3 mJ, the UV pulse is energetic enough to ionize the atmospheric molecules (4 and 3 photons respectively for N_2 and O_2) and create an ionized channel above the sample at short delay times (before 5 ns). During the expansion of the main bubble, the shockwave compress the ambient gas and is enveloped by a layer of gas at high pressure. Such dense gas can absorb efficiently the tailing part of the laser pulse through multiple photon ionization of the air molecules. The ionized layer totally screens the laser pulse preventing it from penetrating into the plasma. At this excited interface, the pressure of the plasma pushes the gas to get out through this and a detonation wave (called a Laser-Supported Detonation Wave, LSDW) expands following the ionized channel at higher velocity.

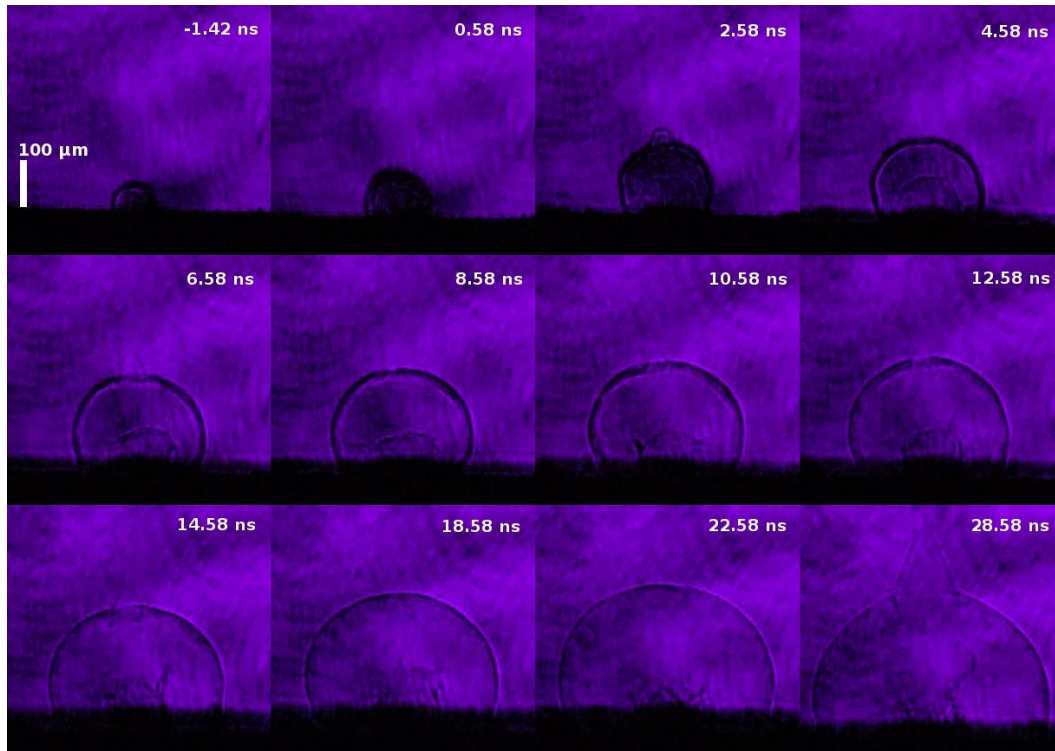


Figure 4. Time evolution of the shockwave induced by the laser ablation of Nylon 6,6 by a UV pulse (266 nm, 4 ns, 3 mJ)

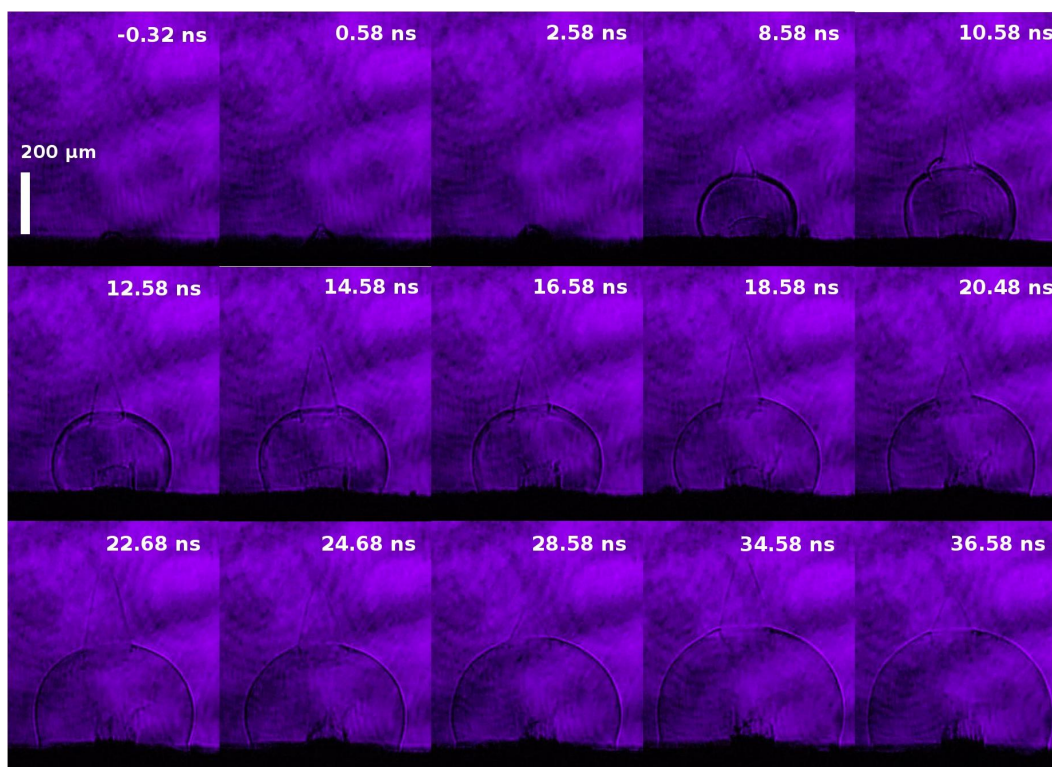


Figure 5. Time evolution of the shockwave induced by the laser ablation of Nylon 6,6 by a UV pulse (266 nm, 4 ns, 5 mJ)

3.2 Time-resolved LIBS

Spectrum from Time-Resolved Laser-induced breakdown spectroscopy of Nylon 6,6 is shown in figure 6.

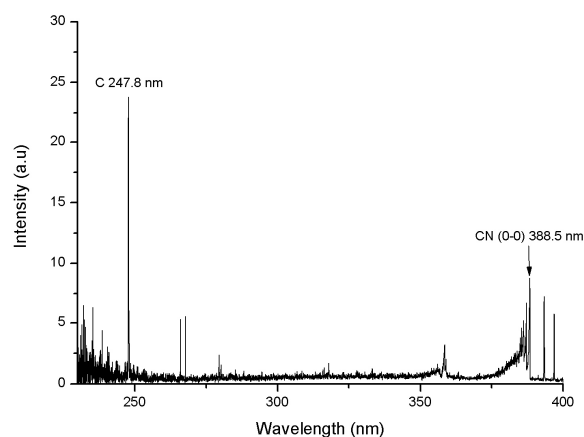


Figure 6. LIBS spectrum of Nylon 6,6 (pulse duration: 5 ns, wavelength: 266 nm, energy: 5 mJ)

We can notice the presence of atomic C (247.8 nm) and the ro-vibrational bands of the molecular species CN (350-390 nm) as expected. However, because of the expansion into the air, the LIBS signal can be modified due to chemical reactions between the excited atmosphere and the ablated species. In order to study this chemistry, time-resolved LIBS has been made. Thanks to this technique, we are able to see the time evolution of the species in the

plasma. For species directly ablated from the sample, we expect an exponential decrease. But for species created in the plasma by chemical reactions, we expect a recombination behavior.

A simple kinetic chemical model has been established from the reaction $2C + N_2 \xrightarrow{k} 2CN$:

$$\begin{cases} \frac{d[C]}{dt} = -k[N_2][C] - v_d^C[C] \\ \frac{d[CN]}{dt} = k[N_2][C] - v_d^{CN}[CN] \end{cases}$$

with k the reaction rate and v_d the diffusion velocity (or extinction rate) of the species in the plasma (taking into account the natural decreasing rate of the emission signal). The concentration of N_2 is taken as a reservoir (atmosphere)

Our study has compared the same regimes than the shadowgraph study: infrared and ultraviolet nanosecond ablation.

3.2.1 Infrared regime of ablation

In figure 7, we see the time evolution of the signal from atomic C and molecular CN species in a plasma induced by a 5 ns, 1064 nm pulse which energy varies from 1 to 5 mJ. We can see that below 3 mJ, the species emit as native species directly ablated. But from 3 to 5 mJ, a recombination behavior is clearly present for the CN signal.

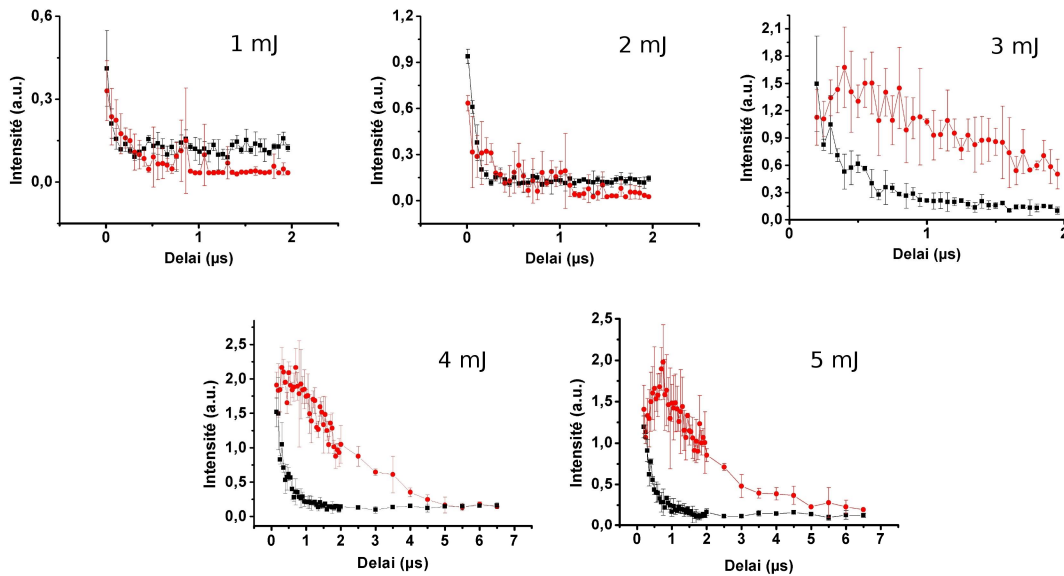


Figure 7. Time evolution of the atomic C (247.9 nm, black line) and molecular CN (388.5 nm, red line) signal from the plasma induced by an IR pulse.

We notice that the initial values of the signals of atomic C and molecular CN increases with the laser pulse energy up to 3 mJ, but above this energy, initial C decreases while CN increases. This behavior shows that, when the pulse energy is less than or equal to 3 mJ, the ablation is efficient and the initial signal is proportional to the amount of energy deposited on the sample. Above this value, the ablation becomes inefficient and so, there is no more ablated matter but the pulse energy seems to be used for the chemical reaction $2C + N_2 \xrightarrow{k} 2CN$.

The reaction rate calculated by fitting the chemical model on curves above 3 mJ is quite constant around $2 \cdot 10^{-7} \text{ ns}^{-1}$ and the extinction rate around $5 \cdot 10^{-4} \text{ ns}^{-1}$. But while the recombination rate is constant, the extinction time of atomic carbon increases suddenly from 75 ns below 3 mJ to 250 ns to reach a plateau above 3 mJ. That means that the atomic

carbon, even if there is no changes in the reaction rate, stays longer in the region seen by the spectrometer. That can be explained by an equilibrium in the chemical reaction, where CN radicals broke and provide 2 atoms of C in the plasma in an excited state, which give signal in the LIBS spectrum.

3.2.2 Ultraviolet regime of ablation

In figure 8, we see the time evolution of the signal from atomic C and molecular CN species in a plasma induced by a 5 ns, 266 nm pulse with energy varied from 1 to 5 mJ. The recombination behavior is also present in this regime but is less visible than in the infrared regime.

The initial signal from C and CN increases from 1 to 2 mJ. The initial CN signal decreases above 3 mJ and reaches a plateau with a value smaller than that for smaller energies. Such a behavior is the consequence of a shielding of the pulse energy above 3 mJ. While the ablation is efficient under 3 mJ, increasing the energy doesn't mean increasing of the ablation matter amount. But this energy is used to enhance the chemical reactions, as we see on the figure 8.

The chemical reaction model used for the IR regime can not be used to fit successfully the experimental curves in the UV regime. This can be explained by the fact that the CN bonds are also generated by other processes than those considered in the model.

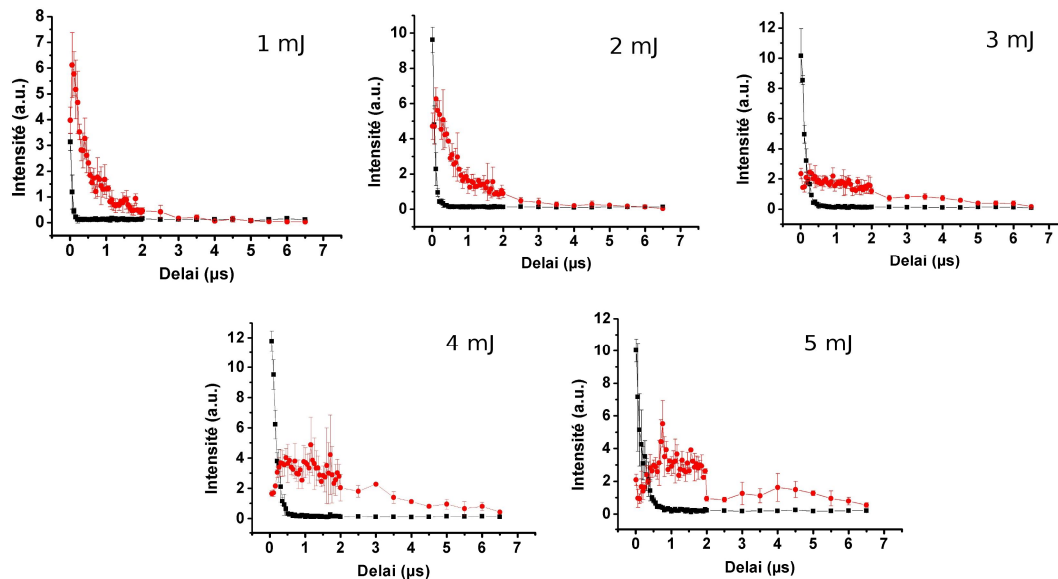


Figure 8. Time evolution of the atomic C (247.9 nm, black line) and molecular CN (388.5 nm, red line) signal from the plasma induced by a UV pulse.

3.3 Correlations between early stage expansion and emission spectrum of the laser induced plasma

The goal of this study is to link the hydrodynamics at the early stage of plasma expansion and its spectroscopic emission. In each analysis, we have denoted different regimes for either the ablation or the plasma emission, showing on one hand a strong interaction of the plasma with the laser pulse and the surrounding atmosphere, and on another hand, a recombination mechanism leading to the creation of CN radicals, both above 3 mJ.

As we have noticed in the discussion on the time-resolved LIBS, the initial signal of the emitters gives an idea about how the pulse energy is used during the ablation. Both regimes shows a screening process above 3 mJ, accompanied by a recombination behavior of the molecular CN species.

In IR regime of ablation, the early stage of expansion shows that the pulse is slightly absorbed by the shockwave and penetrates within the plasma during its expansion. This continuous deposit of energy in the plasma

contributes to its warming and so, to the molecular recombination of CN as we can see on the time-resolved LIBS signal. Even if the pulse energy increases, the recombination rate remains quite constant and the initial signal from the emitters decreases while the axial expansion of the shockwave increases. This means that the additional pulse energy above 3 mJ is only used to heat the plasma and accelerate its expansion.

In UV regime of ablation, the shadowgraph shows the apparition of a Laser-Supported Detonation Wave, created by the absorption of the tail of the pulse by the shockwave at the interface with the air. The strength of this phenomenon (very fast expansion along the laser axis) shows that the energy in the pulse tail is almost totally absorbed and used to induce the detonation wave. That is why the initial signal from the spectroscopic emitters reaches a plateau when this LSDW appears. But we have also seen that, for making this strong absorption possible, the atmospheric molecules have to be ionized, creating by this way a reservoir of reactive compounds (N_2^+ , O_2^+) enhancing the creation of CN radicals by other ways than the simple model we have exposed in this study.

4 CONCLUSION

We have studied the correlation between the hydrodynamic process of early stage expansion of the plasma and its spectroscopic emission. The laser ablation of polymers in the atmosphere with nanosecond pulses leads to a strong interaction between the laser, the plasma and the surrounding atmosphere during the ablation and the plasma expansion. This leads to the screening of the tailing of the laser pulse by the expanding plasma and, as a consequence, to the absorption of its energy. This absorption can only warm the plasma (IR regime) or create a detonation wave (UV regime). As a consequence of this absorption of the pulse by the plasma, a recombination mechanism is enhanced to create CN radicals from the atomic carbon ablated from the sample and the atmospheric excited nitrogen molecules by different ways depending on the ionization of the species involved in the reactions.

The understanding of this correlation allows us to better choose, for the nanosecond ablation regime, the laser parameters for LIBS analysis of polymers. As we can see, for a strong signal from the plasma, avoiding chemical reactions within the plasma allowing the use of CN bands in the analysis, the UV regime (for a photochemical ablation) at low fluence (avoiding the ionization of the atmosphere) could be a good scheme for polymer analysis. The extension to this study are the use of femtosecond laser pulses which do not interact directly with the plasma allowing a more efficient energy deposition on the sample and a more efficient ablation.

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